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FORM PTO 1390 (REV. 10-95) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER: CM2003F

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (if known, see 37 CFR 1.5): 09/889254

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/US99/00800	14 January 1999	

TITLE OF INVENTION: Detergent Tablets Comprising A Pectate Lyase

APPLICANT(S) FOR DO/EO/US: SHOWELL, Michael Stanford et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. [x] This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. [] This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. [] This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(l).
4. [x] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. [x] A copy of the International Application was filed (35 U.S.C. 371(c)(2))
   a. [] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [] has been transmitted by the International Bureau.
   c. [x] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [] A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. [x] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [] have been transmitted by the International Bureau.
   c. [] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [x] have not been made and will not be made.
8. [] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [] A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. [] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [x] A FIRST preliminary amendment.
    [] A SECOND or SUBSEQUENT preliminary amendment.
14. [] A substitute specification.
15. [x] A change of power of attorney and/or address letter.
16. [] Other items or information:

"Express Mail" mailing label number EL 483620561US 650US YCB

Date of Deposit 13 July 2001

I hereby certify that this paper(s) is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to The Assistant Commissioner of Patents, Washington, D.C. 20231

Administrator Mailing Application

Signature Virginia C. Byrd

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
09/889254	PCT/US99/00800	CM2003F

	CALCULATIONS	PTO USE ONLY
ENTER APPROPRIATE BASIC FEE AMOUNT =	$710	
Surcharge of $130.00 for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$0	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	10-20 =	0	x $18.00	$0	
Independent Claims	1-3 =	0	x $80.00	$0	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			$270.00	$0	

TOTAL OF ABOVE CALCULATIONS =	$710	
Processing fee of $130.00 for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).	$0	
TOTAL NATIONAL FEE =	$710	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28,3.31). $40.00 per property +	$0	
TOTAL FEES ENCLOSED =	$710	
	Amount to be refunded	$
	charged	$

a. [ ] A check in the amount of $ ____ to cover the above fees is enclosed.

b. [x] Please charge my Deposit Account No. 16-2480 in the amount of $ 710 to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [x] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 16-2480 . A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

K. L. Waugh, Patent Attorney
Customer Number 27748

Signature

T. David Reed
Name

32,931
Registration Number

Case CM2003F

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the Matter of:

U.S. National Phase Entry
Under 35 USC § 371 from
the International Application of :
SHOWELL, Michael Stanford et al :
Int'l Application No. PCT/US99/00800 :
Filed in the RO/US on 14 January 1999 :
Entitled: DETERGENT TABLETS COMPRISING A PECTATE LYASE

PRELIMINARY AMENDMENT UNDER 37 CFR § 1.112

Assistant Commissioner for Patents
Washington, D.C. 20231
Dear Sir:

Prior to Examination and computation of the fees for entering the captioned International Application into the U.S. National Phase, please preliminarily amend the above-identified application as follows and consider the following Remarks.

AMENDMENTS

IN THE CLAIMS

Please amend Claims as follows:

2. A tablet according to claim 1 wherein the tensile strength of section 1 is larger than the tensile strength of section 2.

3. A tablet according to claims 2 wherein section 2 has a larger exposed surface than section 1.

4. A tablet according to claim 3 wherein section 2 has an exposed surface equal to the exposed surface of the tablet.

5. A tablet according to claim 4 wherein section 2 is applied by a coating process.

6. A detergent tablet according to claim 1 wherein section 1 is a slow dissolving section and section 2 is a rapid dissolving section.

7. A tablet detergent according to claim 1 wherein said pectate lyase is comprised at a level of from 0.0001% to 2% pure enzyme by weight of the tablet.

8. A detergent tablet according to claim 1 wherein more than 70% of the total amount of the pectate lyase enzyme, is comprised in section 2 of the detergent tablet.

9. A tablet detergent according to claim 1 wherein said section 2 comprises a buffering material.

10. A method of cleaning a fabric or a dishware with a tablet according to claim 1.

REMARKS

Claim 1 remain in this application. Claims 2 thru 10 have been amended by eliminating multiple dependent claims and deleting preferably clauses. Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached page is captioned "Version With Markings to Show Changes Made".

The support for these amendments is found in the claims as originally filed. These amendments are being entered to bring the claims into conformance with, *inter alia*, 37 CFR §1.75; no new matter is added.

Respectfully submitted,

By _____

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13 July 2001
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VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the claims:

1. A tablet which comprises a section 1 and a section 2 wherein the section 2 comprises a higher level of pectate lyase than section 1.

2. A tablet according to claim 1 wherein the tensile strength of section 1 is larger[, preferably at least 2% larger, more preferably 5%, even more preferably 10% and most preferably 30%,] than the tensile strength of section 2.

3. A tablet according to claim 2 [claims 1-2] wherein section 2 has a larger exposed surface than section 1.

4. A tablet according to claim 3 [claims 1-3] wherein section 2 has an exposed surface equal to the exposed surface of the tablet.

5. A tablet according to claim 4 [claims 1-4] wherein section 2 is applied by a coating process.

6. A detergent tablet according to claim 1 [any of the preceding claims] wherein section 1 is a slow dissolving section and section 2 is a rapid dissolving section.

7. A tablet detergent according to claim 1 [any of the preceding claims] wherein said pectate lyase is comprised at a level of from 0.0001% to 2%[, more preferably from 0.0005% to 0.1%, most preferred from 0.001% to 0.02%] pure enzyme by weight of the tablet.

8. A detergent tablet according to claim 1 [any of the preceding claims] wherein more than 70%[, preferably more than 85%, more preferably more than 95%] of the total amount of the pectate lyase enzyme, is comprised in section 2 of the detergent tablet.

9. A tablet detergent according to claim 1 [any of the preceding claims] wherein said section 2 comprises a buffering material.

10. A method of cleaning a fabric or a dishware with a tablet according to claim 1 [any of the preceding claims].

DETERGENT TABLETS COMPRISING A PECTATE LYASE

Field of the Invention

The present invention relates to a laundry or automatic dishwashing composition in the tablet form, comprising a pectate lyase.

Background of the invention

Performance of a detergent product is judged by a number of factors, including the ability to remove soils, and the ability to prevent the redeposition of the soils, or the breakdown products of the soils on the articles in the wash. Therefore, detergent compositions include nowadays a complex combination of active ingredients which fulfill certain specific needs. In particular, current detergent formulations generally include detergent enzymes providing cleaning and fabric care benefits.

Removal of stains stemming from plants, wood, mould-clay based soils, muddy soils, and fruits is one of today's toughest cleaning task; especially with the trend toward low wash temperatures. These stains typically contain complex mixtures of fibrous material based mainly on carbohydrates and their derivatives : fibres and cell wall components. Plant based soils are additionally accompanied with amylose, sugars and their derivatives. Food soils are often difficult to remove effectively from a soiled substrate. Highly coloured or "dried-on" soils derived from fruit and/or vegetable juices are particularly challenging to remove. Specific examples of such soils would include orange juice, tomato juice, banana, mango

or broccoli soils. Indeed, pectin polymers are important constituents of plant cell walls. Pectin is a hetero-polysaccharide with a backbone composed of alternating homogalacturonan (smooth regions) and rhamnogalacturonan (hairy regions). The smooth regions are linear polymers of 1,4-linked alpha-D-galacturonic acid. The galacturonic acid residues can be methyl-esterified on the carboxyl group to a varying degree, usually in a non-random fashion with blocks of polygalacturonic acid being completely methyl-esterified. The substrates on which pectin containing stains are commonly found can be fabrics, dishware or hard surfaces.

In addition, the complex nature of everyday "body" soils typically found on pillow cases, T-shirts, collars and socks, provides a continuous thorough cleaning challenge for detergents. These soils are difficult to remove completely due in part to their interaction with the pectin components in the primary cell walls of cotton fibers comprising cotton containing fabrics, and often residues build up on such fabric leading to dinginess and yellowing. Moreover, body fluid stains, such as blood and menstrual fluids, are often difficult to remove effectively from a soiled item, especially when the stains have been aged. Everyday body soils are also found on sanitary and kitchen surfaces such as bathtubs, toilet bowls and dishware.

Therefore, pectin degrading enzymes are known to provide soil/stain removal benefits when used in washing and cleaning operations, specifically to provide the removal of a broad range of plant, dirt, and fruit based stains and enhance the body soil cleaning profile of the detergent compositions. By pectin degrading enzyme it is meant herein any enzyme which acts to break down pectin substances and pectin related substances. Pectin degrading enzymes can be classified according to their preferential substrate, highly methyl-esterified pectin or low methyl-esterified pectin and polygalacturonic acid (pectate), and their reaction mechanism, beta-elimination or hydrolysis. Pectin degrading enzymes can be mainly endo-acting, cutting the polymer at random sites within the chain to give a mixture of oligomers, or they may be exo-acting, attacking from one end of the polymer and producing monomers or dimers. Several pectinase activities acting on the smooth regions of pectin are included in the classification of enzymes provided by the Enzyme Nomenclature (1992) such as pectate lyase (EC 4.2.2.2), pectin lyase (EC 4.2.2.10), polygalacturonase (EC 3.2.1.15), exo-polygalacturonase (EC 3.2.1.67), exo-polygalacturonate lyase (EC 4.2.2.9) and

exo-poly-alpha-galacturonosidase (EC 3.2.1.82). The pectin degrading enzymes are natural mixtures of the above mentioned enzymatic activities.

Each type of pectin degrading enzyme has a unique profile of substrate specificity, activity and stability under different hardness, pH, temperature, surfactant and other detergent ingredient matrix conditions. Pectin degrading enzymes are specifically directed to degrade pectin substances and in particular plant cell walls. In particular, pectate lyase enzymes are directed to the cleavage of α-D-(1,4) glycosidic bonds in poly-D-galacturonans by the mechanism of β-elimination. It is recognised in the art that many pectate lyases are metal ion dependent, in particular Calcium dependent. Therefore, such enzymes may be unstable in a detergent matrix and may lose their activity when calcium is sequestered by builders also present in the detergent matrix. Furthermore, it also known that enzymes lose their maximal activity at high pH in the presence of an oxidising agent like bleach and are degraded by proteases. In summary, when certain pectate lyases are formulated in a detergent matrix comprising high levels of builder, alkalinity, a bleaching system and protease, their enzymatic activity may be significantly decreased unless specific steps are taken to stabilise them. This significantly limits the number of available Pectate Lyases that can be used in detergent applications.

It has been surprisingly found that the cleaning benefits of pectate lyase enzymes can be optimised and maximised with a time controlled release technology. In particular, the time controlled technology is a tablet wherein the pectate lyase is separated from the inhibiting / deactivating other detergent ingredients in a different product phase having a different solubility in the wash. It has been surprisingly found that optimal performance efficiency of the pectate lyase enzyme can be achieved when said enzyme is incorporated into a tablet and such system delivers significant soil and stain cleaning benefits. It has further been found that such time controlled release technology allows a broader range of Pectate Lyases to be used, including those that show a high degree of instability in standard detergent matrices.

Detergent compositions in tablet form are known in the art. It is understood that detergent compositions in tablet form hold several advantages over detergent

compositions in particulate form, such as ease of dosing, handling, transportation and storage.

Detergent tablets are most commonly prepared by pre-mixing components of a detergent composition and forming the pre-mixed detergent components into a tablet using any suitable equipment, preferably a tablet press. Tablets are typically formed by compression of the components of the detergent composition so that the tablets produced are sufficiently robust to be able to withstand handling and transportation without sustaining damage. In addition to being robust, tablets must also dissolve sufficiently fast so that the detergent components are released into the wash water as soon as possible at the beginning of the wash cycle. Prior art already tackled the problem of finding a balance between tablet robustness and tablet dissolution.

One solution has been to design multi-phase tablets. Multi-phase detergent tablets described in the prior art are prepared by compressing a first composition in a tablet press to form a substantially planar first layer. A further detergent composition is then delivered to the tablet press on top of the first layer. This second composition is then compressed to form another substantially planar second layer. Other multi-phase tablets exhibiting differential dissolution are prepared such that the second layer is compressed at a lower force than the first layer resulting in faster dissolution of the second layer.

The use of pectin degrading enzymes in detergents has already been recognised in the art. The use of pectin degrading enzyme is also recognised for the cleaning of contact lenses (US 4,710,313 - J60196724). Enzymes having a pectinase activity are described in DE 36 35 427 to increase the capacity of the detergent for removing inorganic dirt, e.g. sludges, from laundry without damaging the fibres and without discoloration to allow the use of zeolites and polycarbonate builders which have a lower capacity for dispersing inorganic materials than the phosphates. Benefits for the use of pectin degrading enzymes in detergent formulations, particularly those designed for use in laundry,

dishwashing and household cleaning operations have been recognised in WO95/25790. JP 60226599 describes detergent compositions comprising conventional detergent actives and a cellulase and hydrolase such as hemicellulase, pectinase, amylase or protease. The combination of cellulase and hydrolase is said to give a good washing effect on inorganic fouling together with enzymatic activity. WO95/09909 describes an enzyme preparation comprising modified enzymes selected from the group of amylase, lipase, oxidoreductase, pectinase or hemicellulase; the modified enzymes having an improved performance due to an alkaline pI and/or increased surface activity obtained by chemical modification or amino acid substitution. Modified pectin and/or pectolytic and/or hemi-cellulolytic and /or lipolytic enzymes are applied advantageously in the papermaking industry and modified amylase and/or lipase in laundry and dishwashing.

In particular, Pectate lyases have been cloned from different bacterial genera such as *Erwinia*, *Pseudomonas*, *Klebsiella* and *Xanthomonas, Streptomyces, Penicillium, Baceriodes, Thermomonospora, Fusarium, and Aspergillus*. Also from *Bacillus subtilis* (Nasser et al. (1993) FEBS **335**:319-326) and *Bacillus* sp. YA-14 (Kim et al. (1994) Biosci. Biotech. Biochem. **58**:947-949) cloning of a pectate lyase has been described. Purification of pectate lyases with maximum activity in the pH range of 8-10 produced by *Bacillus pumilus* (Dave and Vaughn (1971) J. Bacteriol. **108**:166-174), *B. polymyxa* (Nagel and Vaughn (1961) Arch. Biochem. Biophys. **93**:344-352), *B. stearothermophilus* (Karbassi and Vaughn (1980) Can. J. Microbiol. **26**:377-384), *Bacillus* sp. (Hasegawa and Nagel (1966) J. Food Sci. 31:838-845) and *Bacillus* sp. RK9 (Kelly and Fogarty (1978) Can. J. Microbiol. **24**:1164-1172) has been reported. WO 98/45393 discloses detergent compositions containing protopectinase with remarkable detergency against muddy soiling.

However, the formulation of a pectate lyase into a detergent tablet with time controlled release, for superior cleaning performance, has never been previously recognised.

Summary of the invention

The present invention relates to laundry or automatic dishwashing compositions in the tablet form, comprising a pectate lyase for improved cleaning performance, especially on plant-based and body soils.

Detailed description of the invention

The detergent tablet of the present invention is not only sufficiently robust to withstand handling and transportation, but also at least a portion of which dissolves rapidly in the wash water providing rapid delivery of the pectate lyase enzyme.

It is preferred that at least one phase of the tablet dissolves in the wash water within the first ten minutes, preferably five minutes, more preferably four minutes of the wash cycle of an automatic dishwashing or laundry washing machine. Preferably the washing machine is either an automatic dishwashing or laundry washing machine. The time within which the multi-phase tablet or a phase thereof or a detergent active component dissolves is determined according to DIN 44990 using a dishwashing machine available from Bosch on the normal 65°C washing program with water hardness at 18°H using a minimum of six replicates or a sufficient number to ensure reproducibility.

Preferably, the pectate lyase and buffer materials are incorporated into the rapid dissolving portion of the tablet. Without wishing to be bound by theory, it is believed that the pectate lyase is released earlier than the inhibiting / deactivating other detergent ingredients and that optimum pectate lyase activity is obtained at the beginning of the wash under buffered conditions, allowing the formulation in detergent of pectate lyases in the full range of available pectate lyases. Also contemplated are tablets wherein the pectate lyase is released at different stages of the wash process according to the needs of the pectate lyase application and matrix conditions.

Tablet detergent

The present invention encompasses the following different tablet embodiments :
(a) a tablet which comprises a section 1 and a section 2 wherein the section 2 comprises a higher level of pectate lyase.
(b) a tablet as described in (a) wherein the tensile strength of section 1 is larger, preferably at least 2% larger, more preferably 5%, even more preferably 10% and most preferably 30%, than the tensile strength of section 2.
(c) a tablet according to (a) or (b) wherein section 2 has a larger exposed surface than section 1.
(d) a tablet according to (a), (b) or (c) wherein section 2 has an exposed surface equal to the exposed surface of the tablet.
(e) a tablet wherein section 2 is applied by a coating process.
(f) a tablet according to (a) to (e) wherein section 1 is a slow dissolving section and section 2 is a rapid dissolving section.

By "slow dissolving" it is meant herein a tablet dissolving in more than 10 minutes according to the DIN 44990 method described. By "rapid dissolving" it is meant herein a tablet dissolving within the first ten minutes, preferably five minutes, more preferably four minutes according to the DIN 44990 method described above.

Suitable for the purpose of the present invention are the single and multi-phase detergent tablets for use in automatic dishwashing and laundry, having improved strength, especially on long term storage and excellent dissolution characteristics as described in the co-pending European Application No. 9818716.4 filed 28 August 1998.

Such detergent tablet is not only sufficiently robust to withstand handling and transportation, but also at least a portion of which dissolves rapidly in the wash water providing rapid delivery of the pectate lyase enzyme and buffer materials. It is preferred that at least one phase, preferably section 2, of the tablet dissolves in the wash water within the first ten minutes, preferably five minutes, more preferably four minutes of the wash cycle of an automatic dishwashing or laundry washing machine according to DIN 44990, above.

The detergent tablets of the present invention comprise a first phase and, in multi-phase tablet embodiments, also comprise a second and optional subsequent phases. The first phase is in the form of a shaped body of detergent composition comprising one or more detergent components as described below. Preferred detergent components of the first phase include other builder components, bleach, enzymes and surfactant. The components of the detergent composition are mixed together by, for example admixing dry components or spraying-on liquid components. The components are then formed into a first phase using any suitable compression equipment, but preferably in a tablet press.

In mould embodiments, the first phase is prepared such that it comprises at least one mould in the surface of the shaped body. In a preferred embodiment the mould is created using a specially designed tablet press wherein the surface of the punch that contacts the detergent composition is shaped such that when it contacts and presses the detergent composition it presses a mould, or multiple moulds into the first phase of the multi-phase detergent tablet. Preferably, the mould will have an inwardly concave or generally concave surface to provide improved adhesion to the second phase.

The tablets of the invention can also include one or more additional phases prepared from a composition or compositions which comprise one or more detergent components as described below. At least one phase (herein referred to as a second phase) preferably takes the form of a particulate solid (which term encompasses powders, granules, agglomerates, and other particulate solids including mixtures thereof with liquid binders, meltable solids, spray-ons, etc) compressed either as a layer or into/within the one or more moulds of the first phase of the detergent tablet such that the second phase itself takes the form of a shaped body. Preferred detergent components include builders, colourants, binders, surfactants, disrupting agents and enzymes, in particular Pectate Lyase enzymes. In another preferred aspect of the present invention the second and optional subsequent phases comprise a disrupting agent that may be selected from either a disintegrating agent or an effervescent agent. Suitable disintegrating agents include agents that swell on contact with water or facilitate water influx and/or efflux by forming channels in the detergent tablet. Any known

disintegrating or effervescing agent suitable for use in laundry or dishwashing applications is envisaged for use herein. Suitable disintegrating agent include starch, starch derivatives such as Arbocel (tradename), Vivapur (tradename) both available from Rettenmaier, Nymcel (tradename) available from Metsa-serla , alginates, acetate trihydrate, burkeite, monohydrated carbonate formula $Na_2CO_3.H_2O$, carboxymethylcellulose (CMC), CMC-based polymers, sodium acetate, aluminium oxide. Suitable effervescing agents are those that produce a gas on contact with water. Suitable effervescing agents may be oxygen, nitrogen dioxide or carbon dioxide evolving species. Examples of preferred effervescent agents may be selected from the group consisting of perborate, percarbonate, carbonate, bicarbonate in combination with inorganic acids such as sulphamic acid and/or carboxylic acids such as citric, malic and maleic acid and mixtures thereof.

The components of the detergent composition are mixed together by for example premixing dry components and admixing, preferably by spray-on, liquid components. The components of the second and optional subsequent phases are then compressed to form one or more layers or are fed into and retained within the mould provided by the first phase.

The preferred mould embodiments of the present invention comprises two phases; a first and a second phase. The first phase will normally comprise one mould and the second phase will normally consist of a single detergent active composition. However, it is envisaged that the first phase may comprise more than one mould and the second phase may be prepared from more than one detergent active composition. Furthermore, it is also envisaged that the second phase may comprise more than one detergent active composition contained within one mould. It is also envisaged that several detergent active compositions are contained in separate moulds. In this way potentially chemically sensitive detergent components can be separated in order to avoid any loss in performance caused by components reacting together and potentially becoming inactive or exhausted.

In a preferred aspect of the present invention the first, second and/or optional subsequent phases may comprise a binder. Where present the binder is selected from the group consisting of organic polymers, for example polyethylene

and/or polypropylene glycols having an average molecular weight of from about 1000 to about 12000, especially those of molecular weight 4000, 6000 and 9000, polyvinyl pyrolindone (PVP), especially PVP of molecular weight 90 000, polyacrylates, sugars and sugar derivatives, starch and starch derivatives, for example hydroxy propyl methyl cellulose (HPMC) and carboxy methyl cellulose (CMC); and inorganic polymers, such as hexametaphosphate. The polyethyleneglycol binders are highly preferred herein.

In a preferred aspect of the present invention the first phase constitutes at least 50% of the total tablet weight. More preferably the first phase comprises from 60 to 90%, even more preferably from 70 to 85% and most preferably from 80 to 85% of the total tablet weight. The second and optional subsequent phases comprise less than 40% of the tablet weight. More preferably the second and/or optional subsequent phases comprise between 20 and 30%, most preferably from 8 to 15% of the total tablet weight

The detergent tablets are prepared using any suitable tabletting equipment. Preferably multi-phase tablets herein are prepared by compression in a tablet press capable of preparing a tablet comprising a mould. In a particularly preferred embodiment of the present invention the first phase is prepared using a specially designed tablet press. The punch(es) of this tablet press are modified so that the surface of the punch that contacts the detergent composition has a convex surface.

A first detergent composition is delivered into the die of the tablet press and the punch is lowered to contact and then compress the detergent composition to form a first phase. The first detergent composition is compressed using an applied pressure of at least 250 kg/cm^2, preferably between 350 and 2000 kg/cm^2, more preferably 500 to 1500 kg/cm^2, most preferably 600 to 1200 kg/cm^2. The punch is then elevated, exposing the first phase containing a mould. A second and optionally a subsequent detergent composition(s) comprising the pectate lyase is then delivered into the mould. The specially designed tablet press punch is then lowered a second time to lightly compress the second and optional subsequent detergent composition(s) to form the second and optional subsequent phase(s). In another embodiment of the present invention where an optional subsequent phase is present the optional subsequent phase is prepared

in a subsequent compression step substantially similar to the second compression step described above. The second and optional subsequent detergent composition(s) is compressed at a pressure of preferably less than 350 kg/cm^2, more preferably from 40 to 300 kg/cm^2, most preferably from 70 to 270 kg/cm^2. After compression of the second detergent composition, the punch is elevated a second time and the multi-phase detergent tablet is ejected from the tablet press. Single and multi-layer tablets without moulds can be prepared in a similar manner except using a tablet punch having a planar surface.

The detergent tablets of the invention are prepared by compression of one or more compositions comprising detergent active components. Suitably, the compositions may include a variety of different detergent components including builder compounds, surfactants, enzymes, bleaching agents, alkalinity sources, colourants, perfume, lime soap dispersants, organic polymeric compounds including polymeric dye transfer inhibiting agents, crystal growth inhibitors, heavy metal ion sequestrants, metal ion salts, enzyme stabilisers, corrosion inhibitors, suds suppressers, solvents, fabric softening agents, optical brighteners and hydrotropes. In the following, the proportions of these active components are given by weight of the corresponding composition of active detergent components, unless specified otherwise.

In multi-phase tablets, highly preferred detergent components of the first rapid dissolving phase include builder, enzymes specifically the pectate lyase, buffering agent and disrupting agent. Highly preferred detergent components of the second slower dissolving phase include a builder compound, a surfactant, an enzyme and a bleaching agent.

Builders

Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO_2:Na_2O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $NaMSi_xO_{2x+1}\cdot yH_2O$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:

$M_z(zAlO_2)_y]\cdot xH_2O$

wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot xH_2O$

wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in

the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C_5-C_{20} alkyl and alkenyl succinic acids and salts thereof. A

particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C_{12}-C_{18} monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Surfactants suitable herein include anionic surfactants such as alkyl sulfates, alkyl ether sulfates, alkyl benzene sulfonates, alkyl glyceryl sulfonates, alkyl and alkenyl sulphonates, alkyl ethoxy carboxylates, N-acyl sarcosinates, N-acyl taurates and alkyl succinates and sulfosuccinates, wherein the alkyl, alkenyl or acyl moiety is C_5-C_{20} , preferably C_{10}-C_{18} linear or branched; cationic surfactants such as choline esters (US-A-4228042, US-A-4239660 and US-A-4260529) and mono C_6-C_{16} N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups; low and high cloud point nonionic surfactants and mixtures thereof including nonionic alkoxylated surfactants (especially ethoxy-

lates derived from C_6-C_{18} primary alcohols), ethoxylated-propoxylated alcohols (e.g., Olin Corporation's Poly-Tergent® SLF18), epoxy-capped poly(oxyalkylated) alcohols (e.g., Olin Corporation's Poly-Tergent® SLF18B - see WO-A-94/22800), ether-capped poly(oxyalkylated) alcohol surfactants, and block polyoxyethylene-polyoxypropylene polymeric compounds such as PLURONIC®, REVERSED PLURONIC®, and TETRONIC® by the BASF-Wyandotte Corp., Wyandotte, Michigan; amphoteric surfactants such as the amine oxides and alkyl amphocarboxylicc surfactants such as Miranol™ C2M; and zwitterionic surfactants such as the betaines and sultaines; and mixtures thereof. Surfactants suitable herein are disclosed, for example, in US-A-3,929,678 , US-A- 4,259,217, EP-A-0414 549, WO-A-93/08876 and WO-A-93/08874. Surfactants are typically present at a level of from about 0.2% to about 30% by weight, more preferably from about 0.5% to about 10% by weight, most preferably from about 1% to about 5% by weight of composition.

Enzymes suitable for use in section 1 herein include enzymes like protease, amylase, lipase, cutinase and/or cellulase.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE®, DURAZYM® and SAVINASE® from Novo and MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine protealytic enzyme which is called "Protease A" herein. Suitable is the protease called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is

described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994. Also suitable is a carbonyl hydrolase variant of the protease described in WO95/10591, having an amino acid sequence derived by replacement of a plurality of amino acid residues replaced in the precursor enzyme corresponding to position +210 in combination with one or more of the following residues : +33, +62, +67, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218, and +222, where the numbered position corresponds to naturally-occurring subtilisin from *Bacillus amyloliquefaciens* or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins, such as *Bacillus lentus* subtilisin (co-pending patent application US Serial No. 60/048,550, filed June 04, 1997).

Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221.

See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

The proteolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

The cellulases usable in the present invention include both bacterial or fungal cellulases. Preferably, they will have a pH optimum of between 5 and 12 and a specific activity above 50 CEVU/mg (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, J61078384 and WO96/02653 which discloses fungal cellulase produced respectively from Humicola insolens, Trichoderma, Thielavia and Sporotrichum. EP 739 982 describes cellulases isolated from novel Bacillus species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO95/26398.
Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800.
Other suitable cellulases are cellulases originated from Humicola insolens having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from Humicola insolens, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from Trichoderma longibrachiatum described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and WO91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 and WO95/24471.
Said cellulases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc and with a phenolic substrate as bleach enhancing molecule. They are used for "solution bleaching",

i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.
Enhancers are generally comprised at a level of from 0.1% to 5% by weight of total composition. Preferred enhancers are substitued phenthiazine and phenoxasine 10-Phenothiazinepropionicacid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substitued syringates (C3-C5 substitued alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.
Said peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum var. lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R(Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitables are the lipolytic enzymes described in EP 258

068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.
Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor); WO 90/09446 (Plant Genetic System) and WO 94/14963 and WO 94/14964 (Unilever).
The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Amylases (α and/or ß) can be included for removal of carbohydrate-based stains. WO94/02597, Novo Nordisk A/S published February 03, 1994, describes detergent compositions which incorporate mutant amylases. See also WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in detergent compositions include both α- and β-amylases. α-Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314, published August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases described in EP 277 216, WO95/26397 and WO96/23873 (all by Novo Nordisk).
Examples of commercial α-amylases products are Purafect Ox Am® from Genencor and Termamyl®, Ban® ,Fungamyl® and Duramyl®, all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α-amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α-amylase activity assay. Suitable are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The amylolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimise their performance efficiency in the detergent compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability. Special attention must be paid to the cellulases as most of the cellulases have separate binding domains (CBD). Properties of such enzymes can be altered by modifications in these domains.

Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc. containing one enzyme) or as mixtures of two or more enzymes (e.g. cogranulates).

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in co-pending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful Bacillus, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.bacterial and fungal cellulases such as Carezyme and Celluzyme (Novo Nordisk A/S); peroxidases; lipases such as Amano-P (Amano Pharmaceutical Co.), M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R (Novo); cutinases; proteases such as Esperase^R, Alcalase^R, Durazym^R and Savinase^R (Novo) and Maxatase^R, Maxacal^R, Properase^R and Maxapem^R (Gist-Brocades); and α and β amylases such as Purafect Ox Am^R (Genencor) and Termamyl^R, Ban^R, Fungamyl^R, Duramyl^R, and Natalase^R (Novo); and mixtures thereof. Enzymes are preferably added herein as prills, granulates, or cogranulates at levels typically in the range from about 0.0001% to about 2% pure enzyme by weight of composition.

Bleaching agents suitable herein include chlorine and oxygen bleaches, especially inorganic perhydrate salts such as sodium perborate mono-and tetrahydrates and sodium percarbonate optionally coated to provide controlled rate of release (see, for example, GB-A-1466799 on sulfate/carbonate coatings), preformed organic peroxyacids and mixtures thereof with organic peroxyacid bleach precursors and/or transition metal-containing bleach catalysts (especially manganese or cobalt). Inorganic perhydrate salts are typically incorporated at levels in the range from about 1% to about 40% by weight, preferably from about

2% to about 30% by weight and more preferably from abut 5% to about 25% by weight of composition. Peroxyacid bleach precursors preferred for use herein include precursors of perbenzoic acid and substituted perbenzoic acid; cationic peroxyacid precursors; peracetic acid precursors such as TAED, sodium acetoxybenzene sulfonate and pentaacetylglucose; pernonanoic acid precursors such as sodium 3,5,5-trimethylhexanoyloxybenzene sulfonate (iso-NOBS) and sodium nonanoyloxybenzene sulfonate (NOBS); Phenolsulfonate ester of N-nonanoyl-6-aminocaproic acid (NACA-OBS, described in WO94/28106), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect, amide substituted alkyl peroxyacid precursors (EP-A-0170386); and benzoxazin peroxyacid precursors (EP-A-0332294 and EP-A-0482807). Bleach precursors are typically incorporated at levels in the range from about 0.5% to about 25%, preferably from about 1% to about 10% by weight of composition while the preformed organic peroxyacids themselves are typically incorporated at levels in the range from 0.5% to 25% by weight, more preferably from 1% to 10% by weight of composition. Bleach catalysts preferred for use herein include the manganese triazacyclononane and related complexes (US-A-4246612, US-A-5227084); Co, Cu, Mn and Fe bispyridylamine and related complexes (US-A-5114611); and pentamine acetate cobalt(III) and related complexes(US-A-4810410).

Other suitable components herein include organic polymers having dispersant, anti-redeposition, soil release or other detergency properties invention in levels of from about 0.1% to about 30%, preferably from about 0.5% to about 15%, most preferably from about 1% to about 10% by weight of composition. Preferred anti-redeposition polymers herein include acrylic acid containing polymers such as Sokalan PA30, PA20, PA15, PA10 and Sokalan CP10 (BASF GmbH), Acusol 45N, 480N, 460N (Rohm and Haas), acrylic acid/maleic acid copolymers such as Sokalan CP5 and acrylic/methacrylic copolymers. Preferred soil release polymers herein include alkyl and hydroxyalkyl celluloses (US-A-4,000,093), polyoxyethylenes, polyoxypropylenes and copolymers thereof, and nonionic and anionic polymers based on terephthalate esters of ethylene glycol, propylene glycol and mixtures thereof.

Heavy metal sequestrants and crystal growth inhibitors are suitable for use herein in levels generally from about 0.005% to about 20%, preferably from about

0.1% to about 10%, more preferably from about 0.25% to about 7.5% and most preferably from about 0.5% to about 5% by weight of composition, for example diethylenetriamine penta (methylene phosphonate), ethylenediamine tetra(methylene phosphonate) hexamethylenediamine tetra(methylene phosphonate), ethylene diphosphonate, hydroxy-ethylene-1,1-diphosphonate, nitrilotriacetate, ethylenediaminotetracetate, ethylenediamine-N,N'-disuccinate in their salt and free acid forms.

The compositions herein, especially for use in dishwashing, can contain a corrosion inhibitor such as organic silver coating agents in levels of from about 0.05% to about 10%, preferably from about 0.1% to about 5% by weight of composition (especially paraffins such as Winog 70 sold by Wintershall, Salzbergen, Germany), nitrogen-containing corrosion inhibitor compounds (for example benzotriazole and benzimadazole - see GB-A-1137741) and Mn(II) compounds, particularly Mn(II) salts of organic ligands in levels of from about 0.005% to about 5%, preferably from about 0.01% to about 1%, more preferably from about 0.02% to about 0.4% by weight of the composition.

Other suitable components herein include colourants, water-soluble bismuth compounds such as bismuth acetate and bismuth citrate at levels of from about 0.01% to about 5%, enzyme stabilizers such as calcium ion, boric acid, propylene glycol and chlorine bleach scavengers at levels of from about 0.01% to about 6%, lime soap dispersants (see WO-A-93/08877), suds suppressors (see WO-93/08876 and EP-A-0705324), polymeric dye transfer inhibiting agents, optical brighteners, perfumes, fillers and clay and cationic fabric softeners.

The detergent tablets herein are preferably formulated to have a not unduly high pH, preferably a pH in 1% solution in distilled water of from about 8.0 to about 12.5, more preferably from about 9.0 to about 11.8, most preferably from about 9.5 to about 11.5.

Preferably, the tablet will be the tablets described in the co-pending European application No. 9815525.2 filed 17 July 1998.

Such tablets are multi-phase detergent tablets for use in a washing machine, the tablet comprising:

a) a slower dissolving phase in the form of a shaped body having at least one mould therein (Section 1); and

b) a second rapid dissolving phase in the form of a particulate solid compressed within said mould (Section 2), comprising the pectate lyase enzyme of the present invention.

In preferred embodiments, the first phase is a compressed shaped body prepared at an applied compression pressure of at least about 350 kg/cm^2 (3.43 kN/cm^2), preferably from about 400 to about 2000, especially from about 600 to about 1200 kg/cm^2 (compression pressure herein is the applied force divided by the cross-sectional area of the tablet in a plane transverse to the applied force - in effect, the transverse cross-sectional area of the die of the rotary press). It is also preferred that the particulate solid of the second phase (which terminology is intended to include the possibility of multiple 'second' phases, sometimes referred to herein as 'optional subsequent phases') be compressed into said mould at an applied compression pressure less than that applied to the first phase and preferably at a compression pressure of less than about 350 kg/cm^2, preferably in the range from about 40 kg/cm^2 to about 300 kg/cm^2 and more preferably from about 70 to about 270 kg/cm^2, such tablets being preferred herein from the viewpoint of providing optimum tablet integrity and strength (measured for example by the Child Bite Strength [CBS] test) and product dissolution characteristics. The tablets of the invention preferably have a CBS of at least 10kg, preferably greater than 12kg, more preferably greater than 14kg, CBS being measured per the US Consumer Product Safety Commission Test Specification. Also, the compression pressures applied to the first and second phases will generally be in a ratio of at least about 2:1, preferably at least about 4:1.

Thus, according to a further aspect of the invention, there is provided a multi-phase detergent tablet for use in a washing machine, the tablet comprising:

a) a first slow dissolving phase in the form of a compressed shaped body having at least one mould therein, the shaped body being prepared at a compression pressure of at least about 350 kg/cm^2; and

b) a second phase in the form of a particulate solid compressed within said mould, the second phase being compressed at a pressure of less than about 350 kg/cm^2, comprising the pectate lyase enzyme of the present invention

In other preferred embodiments, the second phase is in the form of a compressed or shaped body adhesively contained, for example by physical or chemical adhesion, within the at least one mould of the first body. It is also preferred that the first and second phases are in a relatively high weight ratio to one another, for example at least about 6:1, preferably at least about 10:1; also that the tablet composition contain one or more detergent actives (for example enzymes, bleaches, bleach activators, bleach catalysts, surfactants, chelating agents etc) which is predominantly concentrated in the second phase, for example, at least about 50%, preferably at least about 60%, especially about 80% by weight of the active (based on the total weight of the active in tablet) is in the second phase of the tablet. In this case specifically the preferred active is the pectate lyase enzyme. Again, such compositions are optimum for tablet strength, dissolution, cleaning, and pH regulation characteristics providing, for example, tablet compositions capable of dissolving in the wash liquor so as to deliver at least 50%, preferably at least 60%, and more preferably at least 80% by weight of the pectate lyase to the wash liquor within 10, 5, 4 or even 3 minutes of the start of the wash process.

Thus, according to another aspect of the invention, there is provided a multi-phase detergent tablet for use in a washing machine, the tablet comprising:

a) slow dissolving first phase in the form of a shaped body having at least one mould therein (Section 1), and

b) a rapid dissolving second phase containing pectate lyase and in the form of a particulate solid compressed within said mould (Section 2),
and wherein section 2 of the tablet comprises at 70%, preferably at least 85%, more preferably at least 95% by weight of the pectate lyase which is delivered to the wash within the first 10 minutes, preferably within the first 5 minutes, and more preferably within the first 3 minutes of the wash process.

Also suitable are the following tablets, specifically designed for laundry purposes :

Tablet Manufacture

Detergent tablets can be prepared simply by mixing the solid ingredients together and compressing the mixture in a conventional tablet press as used, for example, in the pharmaceutical industry. Preferably the principal ingredients, in particular gelling surfactants, are used in particulate form. Any liquid ingredients, for example surfactant or suds suppressor, can be incorporated in a conventional manner into the solid particulate ingredients.
In particular for laundry tablets, the ingredients such as builder and surfactant can be spray-dried in a conventional manner and then compacted at a suitable pressure. Preferably, the tablets according to the invention are compressed using a force of less than 100000N, more preferably of less than 50000N, even more preferably of less than 5000N and most preferably of less than 3000 N. Indeed, the most preferred embodiment is a tablet suitable for laundry compressed using a force of less than 2500N, but tablets for auto dish washing may also be considered for example, whereby such auto dish washing tablets are usually more compressed than laundry tablets.
The particulate material used for making the tablet of this invention can be made by any particulation or granulation process. An example of such a process is spray drying (in a co-current or counter current spray drying tower) which typically gives low bulk densities 600g/l or lower. Particulate materials of higher density can be prepared by granulation and densification in a high shear batch

mixer/granulator or by a continuous granulation and densification process (e.g. using Lodige® CB and/or Lodige® KM mixers). Other suitable processes include fluid bed processes, compaction processes (e.g. roll compaction), extrusion, as well as any particulate material made by any chemical process like flocculation, crystallisation sentering, etc. Individual particles can also be any other particle, granule, sphere or grain.

The components of the particulate material may be mixed together by any conventional means. Batch is suitable in, for example, a concrete mixer, Nauta mixer, ribbon mixer or any other. Alternatively the mixing process may be carried out continuously by metering each component by weight on to a moving belt, and blending them in one or more drum(s) or mixer(s). Non-gelling binder can be sprayed on to the mix of some, or all of, the components of the particulate material. Other liquid ingredients may also be sprayed on to the mix of components either separately or premixed. For example perfume and slurries of optical brighteners may be sprayed. A finely divided flow aid (dusting agent such as zeolites, carbonates, silicas) can be added to the particulate material after spraying the binder, preferably towards the end of the process, to make the mix less sticky.

The tablets may be manufactured by using any compacting process, such as tabletting, briquetting, or extrusion, preferably tabletting. Suitable equipment includes a standard single stroke or a rotary press (such as Courtoy®, Korch®, Manesty®, or Bonals®). The tablets prepared according to this invention preferably have a diameter of between 20mm and 60mm, preferably of at least 35 and up to 55 mm, and a weight between 25 and 100 g. The ratio of height to diameter (or width) of the tablets is preferably greater than 1:3, more preferably greater than 1:2. The compaction pressure used for preparing these tablets need not exceed 100000 kN/m^2, preferably not exceed 30000 kN/m^2, more preferably not exceed 5000 kN/m^2, even more preferably not exceed 3000kN/m^2 and most preferably not exceed 1000kN/m^2. In a preferred embodiment according to the invention, the tablet has a density of at least 0.9 g/cc, more preferably of at least

1.0 g/cc, and preferably of less than 2.0 g/cc, more preferably of less than 1.5 g/cc, even more preferably of less than 1.25 g/cc and most preferably of less than 1.1 g/cc.

Multi layered tablets are typically formed in rotating presses by placing the matrices of each layer, one after the other in matrix force feeding flasks. As the process continues, the matrix layers are then pressed together in the pre-compression and compression stages stations to form the multilayer layer tablet. With some rotating presses it is also possible to compress the first feed layer before compressing the whole tablet.

Hydrotrope compound

In a preferred embodiment of the invention, a highly soluble compound having a cohesive effect is integrated to the tablet of the invention, whereby this compound is also a hydrotrope compound. Such hydrotrope compound may be generally used to favour surfactant dissolution by avoiding gelling, so that they may be for example advantageously comprised in a softer faster dissolving layer which also contains the pectate lyase. A specific compound is defined as being hydrotrope as follows (see S.E. Friberg and M. Chiu, J. Dispersion Science and Technology, 9(5&6), pages 443 to 457, (1988-1989)):

1. A solution is prepared comprising 25% by weight of the specific compound and 75% by weight of water.
2. Octanoic Acid is thereafter added to the solution in a proportion of 1.6 times the weight of the specific compound in solution, the solution being at a temperature of 20°Celsius. The solution is mixed in a Sotax beaker with a stirrer with a marine propeller, the propeller being situated at about 5mm above the bottom of the beaker, the mixer being set at a rotation speed of 200 rounds per minute.
3. The specific compound is hydrotrope if the the Octanoic Acid is completely solubilised, i.e . if the solution comprises only one phase, the phase being a liquid phase.

It should be noted that in a preferred embodiment of the invention, the hydrotrope compound is a flowable material made of solid particles at operating conditions between 15 and 60° Celsius.

Hydrotrope compounds include the compounds listed thereafter:

A list of commercial hydrotropes could be found in McCutcheon's Emulsifiers and Detergents published by the McCutcheon division of Manufacturing Confectioners Company. Compounds of interest also include:

1. Nonionic hydrotrope with the following structure:

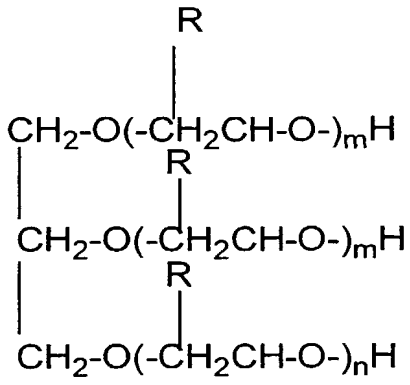
$$R - O - (CH_2CH_2O)_x(CH(CH_3) - CH_2O)_yH$$

where R is a C8-C10 alkyl chain, x ranges from 1 to 15, y from 3 to 10.

2. Anionic hydrotropes such as alkali metal aryl sulfonates. This includes alkali metal salts of benzoic acid, salicylic acid, bezenesulfonic acid and its many derivatives, naphthoic acid and various hydroaromatic acids. Examples of these are sodium, potassium and ammonium benzene sulfonate salts derived from toluene sulfonic acid, xylene sulfonic acid, cumene sulfonic acid, tetralin sulfonic acid, naphtalene sulfonic acid, methyl- naphtalene sulfonic acid, dimethyl naphtalene sulfonic acid, trimethyl naphtalene sulfonic acid=

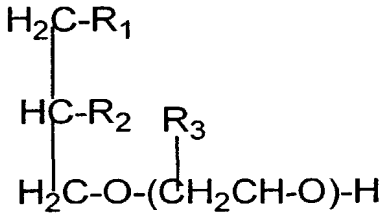
Other examples include salts of dialkyl benzene sulfonic acid such as salts of di-isopropyl benzene sulfonic acid, ethyl methyl benzene sulfonic acid, alkyl benzene sulfonic acid with an alkyl chain length with 3 to 10, (pref. 4 to 9), linear or branched alkyl sulfonates with an alkyl chain with 1 to 18 carbons.

3. Solvent hydrotropes such as alkoxylated glycerines and alkoxylated glycerides, esters slakoxylated glycerines, alkoxylated fatty acids, esters of glycerin, polyglycerol esters. Preferred alkoxylated glycerines have the following structure:



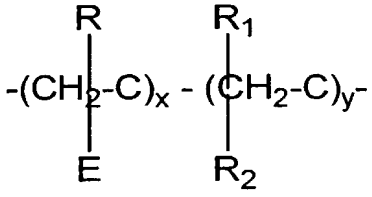
where l, m and n are each a number from 0 to about 20, with l+m+n = from about 2 to about 60, preferably from about 10 to about 45 and R represents H, CH_3 or C_2H_5

Preferred alkoxylated glycerides have the following struture



where R1 and R2 are each C_nCOO or -(CH2CHR$_3$-O)$_l$-H where R_3 = H, CH_3 or C_2H_5 and l is a number from 1 to about 60, n is a number from about 6 to about 24.

4. Polymeric hydrotropes such as those described in EP636687:



where E is a hydrophilic functional group,

R is H or a C1-C10 alkyl group or is a hydrophilic functional group;

R1 is H a lower alkyl group or an aromatic group,

R2 is H or a cyclic alkyl or aromatic group.

The polymer typically has a molecular weight of between about 1000 and 1000000.

5. Hydrotrope of unusual structure such as 5-carboxy-4-hexyl-2-cyclohexene-1-yl octanoic acid (Diacid®)

Use of such compound in the invention would further increase the dissolution rate of the tablet, as a hydrotrope compound facilitates dissolution of surfactants, for example. Such a compound could be formed from a mixture or from a single compound.

Coating

In another embodiment of the present invention, the solidity of the tablet according to the invention may be further improved by making a coated tablet, the coating covering a non-coated tablet according to the invention and containing the pectate lyase enzyme, thereby further improving the mechanical characteristics of the tablet while allowing rapid dissolution of the pectate lyase enzyme.

This very advantageously applies to multi-layer tablets according to the invention, whereby the dissolution characteristics of the outside layer can be tailored to allow fast release of the coating ingredients, thus combining the advantage of the coating with the advantage of time release.

In one embodiment of the present invention, the tablets may be coated so that the tablet does not absorb moisture, or absorbs moisture at only a very slow rate. The coating is also strong so that moderate mechanical shocks to which the tablets are subjected during handling, packing and shipping result in no more than very low levels of breakage or attrition. Finally the coating is preferably brittle so that the tablet breaks up when subjected to stronger mechanical shock. Furthermore it is advantageous if the coating material is dissolved under alkaline conditions, or is readily emulsified by surfactants to allow release of the Pectate Lyase. This also contributes to avoiding the problem of visible residue in the window of a front-loading washing machine during the wash cycle, and also

avoids deposition of undissolved particles or lumps of coating material on the laundry load.

Water solubility is measured following the test protocol of ASTM E1148-87 entitled, "Standard Test Method for Measurements of Aqueous Solubility".

Suitable coating materials that can be used in combination with pectate lyase are dicarboxylic acids. Particularly suitable dicarboxylic acids are selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, tridecanedioic acid and mixtures thereof.

The coating material has a melting point preferably of from 40 °C to 200 °C.

The coating can be applied in a number of ways. However, the preferred method when pectate lyase is contained in the coating is to coat with a solution of the material. In this method, the coating is applied as a solution, the solvent being dried to leave a coherent coating. The substantially insoluble material can be applied to the tablet by, for example, spraying or dipping. Clearly substantially insoluble materials having a melting point below 40 °C are not sufficiently solid at ambient temperatures and it has been found that materials having a melting point above about 200 °C are not practicable to use. Preferably, the materials melt in the range from 60 °C to 160 °C, more preferably from 70 °C to 120 °C.

By "melting point" is meant the temperature at which the material when heated slowly in, for example, a capillary tube becomes a clear liquid.

A coating of any desired thickness can be applied according to the present invention. For most purposes, the coating forms from 1% to 10%, preferably from 1.5% to 5%, of the tablet weight.

The tablet coatings of the present invention are very hard, provide extra strength to the tablet, and allow for early release of the pectate lyase.

In a preferred embodiment of the present invention the fracture of the coating in the wash is improved by adding a disintegrant in the coating. This disintegrant will swell once in contact with water and break the coating in small pieces. This will improve the dissolution of the coating in the wash solution. The disintegrant is

suspended in the coating melt at a level of up to 30%, preferably between 5% and 20%, most preferably between 5 and 10% by weight. Possible disintegrants are described in Handbook of Pharmaceutical Excipients (1986). Examples of suitable disintegrants include starch: natural, modified or pregelatinized starch, sodium starch gluconate; gum: agar gum, guar gum, locust bean gum, karaya gum, pectin gum, tragacanth gum; croscarmylose Sodium, crospovidone, cellulose, carboxymethyl cellulose, algenic acid and its salts including sodium alginate, silicone dioxide, clay, polyvinylpyrrolidone, soy polysacharides, ion exchange resins and mixtures thereof.

Tensile Strength

For the purpose of measuring tensile strength of a layer, the layer may be considered as a tablet itself.

Depending on the composition of the starting material, and the shape of the tablets, the used compacting force may be adjusted to not affect the tensile strength, and the disintegration time in the washing machine. This process may be used to prepare homogenous or layered tablets of any size or shape.

For a cylindrical tablet, the tensile strength corresponds to the diametrical fracture stress (DFS) which is a way to express the strength of a tablet or layer, and is determined by the following equation :

$$\text{Tensile strength} = 2F/\pi Dt$$

Where F is the maximum force (Newton) to cause tensile failure (fracture) measured by a VK 200 tablet hardness tester supplied by Van Kell industries, Inc. D is the diameter of the tablet or layer, and t the thickness of the tablet or layer. For a non round tablet, πD may simply be replaced by the perimeter of the tablet.

(Method Pharmaceutical Dosage Forms : Tablets Volume 2 Page 213 to 217).

A tablet having a diametral fracture stress of less than 20 kPa is considered to be fragile and is likely to result in some broken tablets being delivered to the consumer. A diametral fracture stress of at least 25 kPa is preferred.

This applies similarly to non cylindrical tablets, to define the tensile strength, whereby the cross section normal to the height of the tablet is non round, and whereby the force is applied along a direction perpendicular to the direction of the height of the tablet and normal to the side of the tablet, the side being perpendicular to the non round cross section.

Effervescent

In another preferred embodiment of the present invention the tablets further comprises an effervescent.

Effervescency as defined herein means the evolution of bubbles of gas from a liquid, as the result of a chemical reaction between a soluble acid source and an alkali metal carbonate, to produce carbon dioxide gas,

i.e. $C_6H_8O_7 + 3NaHCO_3 \rightarrow Na_3C_6H_5O_7 + 3CO_2 \uparrow + 3H_2O$

Further examples of acid and carbonate sources and other effervescent systems may be found in : (Pharmaceutical Dosage Forms : Tablets Volume 1 Page 287 to 291).

An effervescent may be added to the tablet mix in addition to the detergent ingredients. The addition of this effervescent to the detergent tablet improves the disintegration time of the tablet. The amount will preferably be between 5 and 20 % and most preferably between 10 and 20% by weight of the tablet. Preferably the effervescent should be added as an agglomerate of the different particles or as a compact, and not as separated particles.

Due to the gas created by the effervescency in the tablet, the tablet can have a higher D.F.S. and still have the same disintegration time as a tablet without effervescency. When the D.F.S. of the tablet with effervescency is kept the same as a tablet without, the disintegration of the tablet with effervescency will be faster.

Further dissolution aid could be provided by using compounds such as sodium acetate or urea. A list of suitable dissolution aid may also be found in

Pharmaceutical Dosage Forms: Tablets, Volume 1, Second edition, Edited by H.A. Lieberman et all, ISBN 0-8247-8044-2.

Other components

Surfactant are comprised in the tablet according to the invention. Suitable surfactants are described herein above. Also suitable for the present tablet are builders, bleaching agents, enzymes and enzymes herein above described

Non gelling binders

Non gelling binders can be integrated to the particles forming the tablet in order to further facilitate dissolution.

If non gelling binders are used, suitable non-gelling binders include synthetic organic polymers such as polyethylene glycols, polyvinylpyrrolidones, polyacrylates and water-soluble acrylate copolymers. The handbook of Pharmaceutical Excipients second edition, has the following binders classification: Acacia, Alginic Acid, Carbomer, Carboxymethylcellulose sodium, Dextrin, Ethylcellulose, Gelatin, Guar gum, Hydrogenated vegetable oil type I, Hydroxyethyl cellulose, Hydroxypropyl methylcellulose, Liquid glucose, Magnesium aluminum silicate, Maltodextrin, Methylcellulose, polymethacrylates, povidone, sodium alginate, starch and zein. Most preferable binders also have an active cleaning function in the laundry wash such as cationic polymers, i.e. ethoxylated hexamethylene diamine quaternary compounds, bishexamethylene triamines, or others such as pentaamines, ethoxylated polyethylene amines, maleic acrylic polymers.

Non-gelling binder materials are preferably sprayed on and hence have an appropriate melting point temperature below 90°C, preferably below 70°C and even more preferably below 50°C so as not to damage or degrade the other active ingredients in the matrix. Most preferred are non-aqueous liquid binders

(i.e. not in aqueous solution) which may be sprayed in molten form. However, they may also be solid binders incorporated into the matrix by dry addition but which have binding properties within the tablet.

Non-gelling binder materials are preferably used in an amount within the range from 0.1 to 15% of the composition, more preferably below 5% and especially if it is a non laundry active material below 2% by weight of the tablet.

It is preferred that gelling binders, such as nonionic surfactants are avoided in their liquid or molten form. Nonionic surfactants and other gelling binders are not excluded from the compositions, but it is preferred that they be processed into the detergent tablets as components of particulate materials, and not as liquids.

The Pectate Lyase enzyme

An essential element of the detergent tablets of the present invention is a pectate lyase enzyme.

Pectate lyase is classified within the classification of enzymes provided by the Enzyme Nomenclature (1992) as EC 4.2.2.2. Said enzyme is known to split the α-1,4,glucoside bond of galacturonic acid found in pectin substances, creating a double bond between C4 and C5 and is substantially free for other pectin degrading activities, i.e having less than 25%, preferably less than 15%, more preferably less than 5% by weight of the enzyme compound of other pectin degrading enzyme activities.

Pectate lyases have been cloned from different bacterial genera such as *Erwinia*, *Pseudomonas*, *Klebsiella* and *Xanthomonas, Streptomyces, Penicillium, Baceriodes, Thermomonospora, Fusarium, and Aspergillus*. Also from *Bacillus subtilis* (Nasser et al. (1993) FEBS **335**:319-326) and *Bacillus* sp. YA-14 (Kim et al. (1994) Biosci. Biotech. Biochem. **58**:947-949) cloning of a pectate lyase has been described. Purification of pectate lyases with maximum activity in the pH range of 8-10 produced by *Bacillus pumilus* (Dave and Vaughn (1971) J. Bacteriol. **108**:166-174), *B. polymyxa* (Nagel and Vaughn (1961) Arch. Biochem. Biophys. **93**:344-352), *B. stearothermophilus* (Karbassi and Vaughn (1980) Can. J. Microbiol. **26**:377-384), *Bacillus* sp. (Hasegawa and Nagel (1966) J. Food Sci.

31:838-845) and *Bacillus* sp. RK9 (Kelly and Fogarty (1978) Can. J. Microbiol. **24**:1164-1172) has been reported. WO 98/45393 discloses detergent compositions containing protopectinase with remarkable detergency against muddy soils.

Further suitable pectate lyases for use in the present invention are the protopectinases having an optimum reaction pH of 7.0 or higher when polygalacturonic acid is used as a substrate such as described in WO98/45393 and the pectic acid lyase having the amino acid sequence SEQ no 1 of EP 870 843 or having such amino acid sequence with one or more amino acid being deleted, added or substituted.

Preferred are the pectate lyase enzymes described in the international co-pending application PCT/DK98/00515, first filed in Denmark on November 24, 1997 :

- A pectate lyase comprising a first amino acid sequence consisting of seven (7) amino acid residues having the following sequence: Asn Leu Asn Ser Arg Val Pro (NLNSRVP);
- A pectate lyase which is :

  i) a polypeptide produced by *Bacillus agaradhaerens*, NCIMB 40482 or DSM 8721, or by a *Bacillus* species having a 16S rDNA sequence homology to *Bacillus agaradhaerens*, DSM 8721, of at least 99%, or

  ii) a polypeptide comprising an amino acid sequence as shown in positions 27-359 of SEQ ID NO:2 of PCT/DK98/00515, or

  iii) an analogue of the polypeptide defined in i) or ii) which is at least 45% homologous with said polypeptide, or

  iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 240, and optionally also the arginine in position 245, is conserved and the derived polypeptide is at least 42% homologous with said polypeptide, or

  v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form;

- A pectate lyase which is :

i) a polypeptide produced by *Bacillus licheniformis*, ATCC 14580, or by a *Bacillus* species having a 16S rDNA sequence homology to *Bacillus licheniformis*, ATCC 14580, of at least 99%, or

ii) a polypeptide comprising an amino acid sequence as shown in positions 28-341 of SEQ ID NO:4 of PCT/DK98/00515, or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 45% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 233, and optionally also the arginine in position 238, is conserved and the derived polypeptide is at least 42% homologous with said polypeptide, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form;

- A pectate lyase which is :

i) a polypeptide produced by a *Bacillus* species having the 16S rDNA sequence of SEQ ID NO:14 or by a *Bacillus* species having a 16S rDNA sequence homology to SEQ ID NO:14 higher than 97.3%; or

ii) a polypeptide comprising an amino acid sequence as shown in positions 181-509 of SEQ ID NO:6, or

iii) an analogue of the polypeptide defined in i) which is at least 50% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 390, and optionally also the arginine in position 395, is conserved and the derived polypeptide is at least 44% homologous with said polypeptide, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form,

- A pectate lyase which is :

i) a polypeptide produced by the species *Bacillus halodurans*, or

ii) a polypeptide comprising an amino acid sequence as shown in positions 42-348 of SEQ ID NO:8 of PCT/DK98/00515, or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 45% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 240, and optionally also the arginine in position 245, is conserved and the derived polypeptide is at least 40% homologous with said polypeptide, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form,

- A pectate lyase which is

i) a polypeptide produced by a *Bacillus* species having the 16S rDNA sequence of SEQ ID NO:13 PCT/DK98/00515or by a *Bacillus* species having a 16S rDNA sequence homology to SEQ ID NO:13 of PCT/DK98/00515higher than 98.1%; or

ii) a polypeptide comprising an amino acid sequence as shown in positions 25-335 of SEQ ID NO:10 of PCT/DK98/00515, or

iii) an analogue of the polypeptide defined in i) or which is at least 45% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 227, and optionally also the arginine in position 232, is conserved and the derived polypeptide is at least 41% homologous with said polypeptide, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Similarly preferred is the pectate lyase enzyme described in the international co-pending application PCT/DK98/00514, first filed in Denmark on November 24, 1997 and which is :

i) a polypeptide produced by *Bacillus licheniformis*, ATCC 14580, or

ii) a polypeptide comprising an amino acid sequence as shown in positions 28-221 of SEQ ID NO:4 of PCT/DK98/00514, or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 60% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the lysines in positions 133 and 155 and the arginine in position 158 are conserved and the derived polypeptide is at least 66% homologous with positions 60-158 of SEQ ID NO:4 of PCT/DK98/00514, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

More preferred pectate lyases for the purpose of the present invention are those having optimum activity at pH's >7.0 and derived from Streptomyces fradiae, Streptomyces nitrosporeus, Erwinia carotovora, Bacillus spheroides, Thermomonospora fusca, Pseudomonas solanacearum, Bacteroides thetaiotaomicron, Fusarium solani, Xanthomonas campestris, Bacillus agaradhaerens, and/or Bacillus licheniformis.

Most preferred pectate lyase for the purpose of the present invention is the Pectate lyase from *Bacillus agaradhaerens*, NCIMB 40482 or DSM 8721.

The pectate lyase is incorporated into the tablet of the invention preferably at a level of from 0.0001% to 2%, more preferably from 0.0005% to 0.1%, most preferred from 0.001% to 0.02% pure enzyme by weight of the composition. Preferably more than 70%, more preferably more than 85%, most preferably more than 95% of the total amount of the pectate lyase enzyme will be comprised in section 2 of the detergent tablet of the present invention.

The pectate lyase of the invention, in addition to the enzyme core comprising the catalytically domain, may also contain a cellulose binding domain (CBD), the cellulose binding domain and enzyme core (the catalytically active domain) of the enzyme being operably linked. The cellulose binding domain (CBD) may exist as an integral part of the encoded enzyme, or a CBD from another origin may be

introduced into the enzyme thus creating an enzyme hybrid. In this context, the term "cellulose-binding domain" is intended to be understood as defined by Peter Tomme et al. "Cellulose-Binding Domains: Classification and Properties" in "Enzymatic Degradation of Insoluble Carbohydrates", John N. Saddler and Michael H. Penner (Eds.), ACS Symposium Series, No. 618, 1996. This definition classifies more than 120 cellulose- binding domains into 10 families (I-X), and demonstrates that CBDs are found in various enzymes such as cellulases, xylanases, mannanases, arabinofuranosidases, acetyl esterases and chitinases. CBDs have also been found in algae, e.g. the red alga Porphyra purpurea as a non-hydrolytic polysaccharide-binding protein, see Tomme et al., op.cit. However, most of the CBDs are from cellulases and xylanases, CBDs are found at the N and C termini of proteins or are internal. Enzyme hybrids are known in the art, see e.g. WO 90/00609 and WO 95/16782, and may be prepared by transforming into a host cell a DNA construct comprising at least a fragment of DNA encoding the cellulose- binding domain ligated, with or without a linker, to a DNA sequence encoding the pectate lyase enzyme and growing the host cell to express the fused gene. Enzyme hybrids may be described by the following formula:

CBD - MR - X

wherein CBD is the N-terminal or the C-terminal region of an amino acid sequence corresponding to at least the cellulose binding domain; MR is the middle region (the linker), and may be a bond, or a short linking group preferably of from about 2 to about 100 carbon atoms, more preferably of from 2 to 40 carbon atoms; or is preferably from about 2 to about 100 amino acids, more preferably of from 2 to 40 amino acids; and X is an N-terminal or C-terminal region of the pectate lyase of the invention.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimise their performance efficiency in the detergent compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the

variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing metal binding sites to increase chelant stability.

Preferably, the detergent tablets of the present invention will comprise a buffering agent together with the pectate lyase enzyme. Such buffering agents might be required to generate the optimum pH for activity of the pectate lyase. Any standard buffering agent can be used. Preferred are those having optimum buffer capacity at the pH where the pectate lyase shows optimum activity. Examples include NaH2PO4, NaHCO3, Na2CO3 and Citric Acid, tris(Hydroxymethyl)aminomethane (Trizma (TM) from Sigma), triethanol amine, NN,bis(2-Hydroxyethyl)glycine, N-tris(Hydroxymethyl)methyl-3-aminopropane-sulfonic acid and/or mixtures thereof. Such buffering agent is typically present at 5% or less by weight of the rapid, pectate lyase containing-dissolving phase."

Method of washing

The compositions of the invention may be used in essentially any washing or cleaning methods, including soaking methods, pretreatment methods and methods with rinsing steps for which a separate rinse aid composition may be added.

The process of the invention is conveniently carried out in the course of the cleaning process. The method of cleaning is preferably carried out at 5°C to 95°C, especially between 10°C and 60°C. The pH of the treatment solution is preferably from 7 to 12.

A preferred machine dishwashing method comprises treating soiled articles selected from crockery, glassware, silverware, metallic items, cutlery and

mixtures thereof, with an aqueous liquid having dissolved or dispensed therein an effective amount of a the herein described compositions. By an effective amount is meant from 8g to 60g of product dissolved or dispersed in a wash solution of volume from 3 to 10 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine dishwashing methods. Preferably the detergent tablets are from 15g to 40g in weight, more preferably from 20g to 35g in weight.

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of the herein described compositions. By an effective amount is meant from 20g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

Examples

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

Dishwashing Examples

In examples I-IV, the abbreviated component identifications in the detergent compositions have the following meanings, and all levels are quoted as parts by weight:

STPP	:	Sodium tripolyphosphate: 50% hexahydrate, 6% Phase I and 44% Phase II
Bicarbonate	:	Sodium hydrogen carbonate
Citric Acid	:	Anhydrous Citric acid
Carbonate	:	Anhydrous sodium carbonate
Silicate	:	Amorphous Sodium Silicate (SiO_2:Na_2O ratio = 2.0)
SKS-6	:	Crystalline layered silicate of formula δ-$Na_2Si_2O_5$

PB1	:	Anhydrous sodium perborate monohydrate
Nonionic	:	C_{13}-C_{15} mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5, sold under the tradename Plurafac by BASF
TAED	:	Tetraacetyl ethylene diamine
HEDP	:	Ethane 1-hydroxy-1,1-diphosphonic acid
PAAC	:	Pentaamine acetate cobalt (III) salt
Paraffin	:	Paraffin oil sold under the tradename Winog 70 by Wintershall.
Protease	:	Proteolytic enzyme sold under the tradename Savinase, Alcalase, Durazym by Novo Nordisk A/S, Maxacal, Maxapem sold by Gist-Brocades and proteases described in patents WO91/06637 and/or WO95/10591 and/or EP 251 446.
Amylase	:	Amylolytic enzyme sold under the tradename Purafact Ox Am®described in WO 94/18314, WO96/05295 sold by Genencor; Termamyl®, Fungamyl® and Duramyl®, all available from Novo Nordisk A/S and those described in WO95/26397 (sold under the tradename Natalase By Novo Nordisk).
Pectate Lyase	:	Pectate Lyase from *Bacillus agaradhaerens*, NCIMB 40482 or DSM 8721
BTA	:	Benzotriazole
Sulphate	:	Anhydrous sodium sulphate.
PEG 3000	:	Polyethylene Glycol molecular weight approximately 3000 available from Hoechst
PEG 6000	:	Polyethylene Glycol molecular weight approximately 6000 available from Hoechst

The following illustrates examples detergent tablets of the present invention suitable for use in a dishwashing machine.

I	II	III	IV	V	VI

	I	II	III	IV	V	VI
Phase 1						
STPP	9.6	9.6	10.4	9.6	9.6	11.5
Silicate	0.5	0.7	1.6	1.0	1.0	2.4
SKS-6	1.5	1.5	-	2.3	2.25	
Carbonate	2.3	2.7	3.5	3.6	4.1	5.2
HEDP	0.2	0.2	0.2	0.3	0.3	0.3
PB1	2.4	2.4	2.4	3.7	3.7	3.7
PAAC	0.002	0.002	0.002	0.003	0.004	0.004
Amylase	0.1	0.1	0.11	0.2	0.2	0.2
Protease	0.06	0.06	0.06	0.09	0.09	0.09
Nonionic	0.4	0.8	0.8	1.2	1.2	1.2
PEG 6000	0.4	0.26	0.26	0.4	0.4	0.4
BTA	0.04	0.04	0.04		0.06	0.06
Paraffin	0.1	0.10	0.10	0.1	0.1	0.15
Perfume	0.02	0.02	0.02	0.01	0.01	0.01
Sulphate				0.5	0.05	2.8
Total	17.7g	18.5g	19.6g	23.0g	23.0g	23.0g
Phase 2						
Pectate Lyase	0.005	0.50	0.001	0.002	0.02	0.001
Amylase	0.003	0.003	0.002	0.003	0.003	0.002
Protease	0.01	0.009	0.01	0.01	0.009	0.01
Citric acid	0.3	-	0.3	0.3	-	0.30
Sulphamic acid	-	0.3	-	-	0.3	-
Bicarbonate	1.1	0.4	0.4	1.1	0.4	0.4
Carbonate	-	0.5	-	-	0.5	-
Silicate	-	-	0.6	-	-	0.6
$CaCl_2$	-	0.07	-	-	0.07	-
PEG 3000	0.06	0.06	0.06	0.06	0.06	0.06
Total	2.05g	2.50g	2.1g	2.20g	2.02g	2.15g

The tablet compositions are prepared as follows. The detergent active composition of phase 1 is prepared by admixing the granular and liquid components and is then passed into the die of a conventional rotary press. The press includes a punch suitably shaped for forming a mould. The cross-section of the die is approximately 30x38 mm. The composition is then subjected to to a compression force of 940 kg/cm^2 and the punch is then elevated exposing the

first phase of the tablet containing the mould in its upper surface. The detergent active composition of phase 2 is prepared in similar manner and is passed into the die. The particulate active composition is then subjected to a compression force of 170 kg/cm^2, the punch is elevated, and the multi-phase tablet ejected from the tablet press. The resulting tablets dissolve or disintegrate in a washing machine as described above within 12 minutes, phase 2 of the tablets dissolving within 5 minutes. The tablets display improved strength, especially on long-term storage, together with excellent dissolution characteristics.

Examples VII to XI

The following automatic dishwashing tablets were made in accordance with the present invention (g of raw material and enzymes are expressed in pure enzyme) :

	VII	VIII	IX	X	XI
Tablet body					
STPP	10.3	9.5	10.6	10.6	10.1
Carbonate	5.2	5.2	2.8	3.5	3.5
Silicate	2.4	1.6	2.9	1.6	1.1
SKS-6	2.2	2.2	-	1.5	1.5
HEDP	0.3	0.3	0.2	0.2	0.2
Protease	0.003	0.003	0.002	0.002	0.002
Amylase	0.001	0.001	0.001	0.001	0.001
Perborate	3.7	3.7	2.8	2.4	2.4
C13-15 EO/PO nonionic	1.2	0.9	0.4	0.8	0.6
PEG4000	0.4	-	-	0.3	-
PEG6000	-	0.4	-	-	0.3
BTA	0.09	0.09	0.06	0.06	0.06
Parafin	0.1	0.1	0.1	0.1	0.1
Perfume	-	-	0.02	0.02	0.02
Tablet body total	26.4	24.5	20.1	21.3	20.1
Dimple					

	VII	VIII	IX	X	XI
Protease	0.01	0.01	0.01	0.01	0.01
Amylase	0.003	0.003	0.004	0.003	0.003
Pectate lyase	0.2	0.05	0.2	0.3	0.3
Citric	0.2	0.2	0.6	0.2	0.2
Bicarbonate	0.6	0.6	0.6	0.6	0.6
Triacetin	-	-	1.2	-	-
PEG400	0.02	0.02	-	0.02	0.02
PEG6000	0.08	0.08	-	0.08	0.08
PEG6000	-	-	1.2	-	-
CaCl2	-	-	0.1	-	-
Dimple total	1.5	1.5	3.5	1.5	1.5
Total tablet	27.9	26.0	23.6	22.8	21.6

The following illustrates examples of detergent tablets of the present invention suitable for use in a laundry machine.

i) Detergent powder of compositions I-IV (see tables under) was prepared as follows: all the particulate materials of base composition were mixed together in a mixing drum or spray drum to form a homogenous particulate mixture. During this mixing the spray-on of the binder system was carried out. After this stage, the matrix was separated in two different samples. The DIBS sticky hydrotope was added to only one of the samples and then processed independently in a Loedige KM 600®. The layer with DIBS was used for a harder bottom layer and the layer without DIBS was used for a softer top layer of a dual layer tablet.

ii) Using a Bonals® rotary press both matrices were filled in two independent force feeding flasks. The matrix with DIBS is consecutively filled first in the turret stations, followed by the second matrix (the without DIBS matrix). Both

layers are compressed together in the pre-compression and compression stations to form a dual layer tablet with a harder bottom layer.

iii) In this particular example, the tablets have a rectangular cross section of 62.5 by 38.5 mm, a height of 20.5 mm and a weight of 48 gr. The height of the bottom layer corresponded to 25% of the total height of the tablet. If a round tablet is made of the bottom layer matrix with the same density as in the rectangular tablet (983 g/l), the tensile strength of the layer is 7.8 kPa. Using the same experiment (for a density of 991 g/l), the top layer of the tablet has an equivalent tensile strength of 5.1 kPa. Elasticity measurements gave values of 1.8 J/kN for the top layer and 3.3 J/kN for the bottom layer.

Presented below are Examples for base particulate material composition for making laundry detergent tablets according to the invention, whereby a harder layer may be more compressed than a softer layer, or whereby different compositions may be used or adapted for each layer.

The enzymes levels are expressed by pure enzyme by weight of the total composition and unless otherwise specified, the detergent ingredients are expressed by weight of the total compositions.

	I	II	III	IV
Anionic Agglomerates 1	21.0	21.0	8.6	31.5
Anionic Agglomerates 2	12.6	12.6	22.0	-
Nonionic agglomerates	-	-	9.1	-
Cationic Agglomerate	5.4	5.4	4.6	5.0
Layered Silicate	10.8	10.8	9.7	11.5
Sodium percarbonate	14.2	14.2	12.2	16.2
Bleach activator agglomerates	5.5	5.5	6.1	4.7
Sodium carbonate	13.8	12.6	7.3	3.3
Sodium bicarbonate	-	-	-	2.0
Sodium sulfate	-	-	-	2.4
EDDS/Sulphate particle	0.5	0.5	0.5	0.5

	I	II	III	IV
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.7	0.7	0.6	0.8
Soil Release Polymer	0.3	0.3	0.3	0.3
Fluorescer	0.2	0.2	0.2	0.1
Zinc Phthalocyanide sulphonate encapsulate	0.02	0.02	0.03	0.02
Soap powder	1.4	1.4	1.2	-
Suds Suppressor	1.9	1.9	2.8	2.1
Citric acid	7.1	7.1	5.5	2.0
Pectate Lyase	0.008	0.008	0.001	0.01
Protease	0.03	0.03	0.04	0.03
Lipase	0.003	0.003	0.004	0.0003
Cellulase	0.0001	0.0001	0.0001	0.0001
Amylase	0.009	0.09	0.009	0.005
Binder Spray-on-system 1	1.3	2.5	-	-
Binder Spray-on-system 2	-	-	3.05	-
Polymer particle	-	-	-	3.0
Nonionic spray-on system	-	-	-	5.2
Zeolite	-	-	-	6.2
Perfume Spray-on	-	-	0.5	0.3
Perfume encapsulates	-	-	-	0.2
Sodiumdi isoalkylbenzene sulfonate	-	-	2.1	
TOTAL	100.00	100.00	100.00	100.00

Anionic agglomerates 1 comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate.

Anionic agglomerates 2 comprise of 40% anionic surfactant, 28% zeolite and 32% carbonate.

Nonionic agglomerate comprise 26% nonionic surfactant, 6% Lutensit K-HD 96, 40% Sodium acetate anhydrous, 20% carbonate and 8% zeolite.

Cationic agglomerates comprise of 20% cationic surfactant, 56% zeolite and 24% sulphate.

Layered silicate comprises of 95% SKS 6 and 5% silicate.

Bleach activator agglomerates comprise of 81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.

Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

Zinc phthalocyanine sulphonate encapsulates are 10% active.

Suds suppressor comprises of 11.5% silicone oil (ex Dow Corning); 59% of zeolite and 29.5% of water.

Binder spray-on system 1 comprises of 50% Lutensit K-HD 96 and 50% PEG (polyethylene glycol).

Binder spray-on system 2 comprises of 0.5 parts of Lutensit K-HD 96 and 2.5 parts of PEGs.

Perfume encapsulates comprise 50% perfume and 50% starch.

Polymer particle comprises 36%, 54% zeolite and 10% water

The Nonionic spray-on system comprises of 67% C12-C15 AE5 (alcohol with an average of 5 ethoxy groups per molecule), 24% N-methyl glucose amide and 9% water.

Protease is selected from: proteolytic enzyme sold under the tradename Savinase, Alcalase, Durazym by Novo Nordisk A/S, Maxacal, Maxapem sold by Gist-Brocades and proteases described in patents WO91/06637 and/or WO95/10591 and/or EP 251 446 and/or mixutres thereof.

Amylase is selected from: Amylolytic enzyme sold under the tradename Purafact Ox Am^{R} described in WO 94/18314, WO96/05295 sold by Genencor; Termamyl ®, Fungamyl® and Duramyl®, all available from Novo Nordisk A/S and those described in WO95/26397(Sold under the tradename Natalase by Novo Nordisk A/S) and/or mixtures thereof.

Lipase is selected from: Lipolytic enzyme sold under the tradename Lipolase, Lipolase Ultra by Novo Nordisk A/S and Lipomax by Gist-Brocades, and/or mixutres thereof.

Pectate lyase from *Bacillus agaradhaerens*, NCIMB 40482 or DSM 8721.

Cellulase is selected from: Cellulytic enzyme sold under the tradename Carezyme, Celluzyme and/or Endolase by Novo Nordisk A/S; and/or mixtures thereof.

CLAIMS

1. A tablet which comprises a section 1 and a section 2 wherein the section 2 comprises a higher level of pectate lyase than section 1.

2. A tablet according to claim 1 wherein the tensile strength of section 1 is larger, preferably at least 2% larger, more preferably 5%, even more preferably 10% and most preferably 30%, than the tensile strength of section 2.

3. A tablet according to claims 1-2 wherein section 2 has a larger exposed surface than section 1.

4. A tablet according to claims 1-3 wherein section 2 has an exposed surface equal to the exposed surface of the tablet.

5. A tablet according to claims 1-4 wherein section 2 is applied by a coating process.

6. A detergent tablet according to any of the preceding claims wherein section 1 is a slow dissolving section and section 2 is a rapid dissolving section.

7. A tablet detergent according to any of the preceding claims wherein said pectate lyase is comprised at a level of from 0.0001% to 2%, more preferably from 0.0005% to 0.1%, most preferred from 0.001% to 0.02% pure enzyme by weight of the tablet.

8. A detergent tablet according to any of the preceding claims wherein more than 70%, preferably more than 85%, more preferably more than 95% of the total amount of the pectate lyase enzyme, is comprised in section 2 of the detergent tablet.

9. A tablet detergent according to any of the preceding claims wherein said section 2 comprises a buffering material.

10. A method of cleaning a fabric or a dishware with a tablet according to any of the preceding claims.

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(54) **Title:** DETERGENT TABLETS COMPRISING A PECTATE LYASE

(57) **Abstract**

The present invention relates to a laundry or automatic dishwashing composition in tablet form, comprising a pectate lyase, for improved cleaning performance.

DECLARATION COMBINED WITH POWER OF ATTORNEY

Attorney Docket No.2003

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled _____

the specification of which

(check one) [] is attached hereto.

[] was filed on 14 January 1999 as United States Application No. or PCT International Application Serial No. US99/00800

and was amended on _____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations §1.56.

I hereby claim foreign priority benefits under Title 35 United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)			Priority Claimed	
(Number)	(Country)	(Day/Month/Year Filed)	[] Yes	[] No

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

Application Serial No.	Filing Date	Application Serial No.	Filing Date

I hereby claim the benefit under Title 35 United States Code §120 of any United States application(s), or §365(c) of any PCT International application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35 United States Code §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (If applicable)

As named inventor, I hereby appoint the following registered practitioner(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Respectfully submitted for Applicants,

By _____
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